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(54) Title: CONTROLLED NUCLEATION OF SEMI-CRYSTALLINE POLYMERS (57) Abstract <p>The crystallization onset temperature of a semi-crystalline thermoplastic polymer is increased by melt blending the semi-crystalline thermoplastic polymer with at least one diluent polymer having about the same melting point as, and a density greater than or equal to, that of the semi-crystalline polymer forming a polymer blend. For example, the crystallization onset temperature of linear low density polyethylene is increased by blending it with a minor amount of high density polyethylene. Films formed from these new polymer blends have improved optical and/or mechanical properties and blown bubble stability in spite of increased throughput rate.</p>		

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CONTROLLED NUCLEATION OF SEMI-CRYSTALLINE POLYMERS

This invention relates to thermoplastic polymer blends having increased crystallization onset temperature. The polymer blends are made by blending specific portions of at least one diluent polymer with a semi-crystalline polymer. The semi-crystalline polymers most preferred are linear polyethylene polymers. The preferred diluent polymers are high density polyethylene polymers.

Thermoplastic polymers can be classified as semi-crystalline (at least partly crystalline), highly crystalline, or wholly or mainly amorphous. Crystalline or semi-crystalline polymers typically have a distinct melting point, as measured by differential scanning calorimetry (DSC). Crystalline and semi-crystalline polymers are typically melt-processed into fibers, films or molded articles.

The nucleation and crystallization rates of the polymers during melt processing is important in determining the physical properties of the finished article. If the nucleation rate is low and uneven, the resultant product properties will have wide variation. In addition, low nucleation rates result in lower production capacity.

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In a production environment such as a blown film line or fiber spinning line, a "freeze line" or "frost line" can sometimes be seen, indicating the point of solidification and crystallization. The polymer is still partially molten and tacky prior to the freeze line. If the polymer product comes into contact with other pieces of the production equipment before solidification, the polymer product can stick and create a premature shut down of the manufacturing process. Production capacity reaches its maximum when the freeze line is at the point of sticking to some part of the equipment. By lowering the freeze line, polymer throughput can be increased such that the freeze line is at its the previous level.

The freeze line can be relocated (i.e., lowered) by changing the quenching or cooling conditions. but equipment limitations (e.g., maximum air flow and temperature) can limit the crystallization kinetics of a particular polymer on a particular type of equipment. Other techniques for controlling the freeze line, or crystallization rate involve changing the polymer by adding nucleating agents (e.g., inactive (physical) or active (chemical)) or completely changing polymers. Physical nucleating agents are typically finely divided particles and have a melting and freezing temperature greater than that of the polymer in which the particles are utilized while the chemical nucleating agents are primarily combinations of acidic and basic compounds such as organic or inorganic compounds.

Measurement and control of nucleation and crystallization rates are difficult in commercial processes. Laboratory analytical techniques are available to quantify polymer nucleation and crystallization rates. Onset of crystallization

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temperature is indicative of the ability of a polymer to nucleate and crystallize. The onset of crystallization temperature can be measured by non-isothermal crystallization kinetics using a DSC. Typically, smaller and more uniform spherulites or crystallites are formed at higher crystallization temperatures for thermoplastic polymers. Addition of inactive or physical nucleating agents can increase the crystallization onset temperature, causing the polymer to crystallize earlier (i.e., at a higher temperature) during cooling and to form more uniform crystallites/spherulites in the cooling polymer melt. This, in turn, yields polymer products which have more uniform properties (e.g., optical properties) with fewer deviations and greater predictability. This is illustrated by A.G.M. Last, in Nucleation Effects in High Polymers (Journal of Polymer Science, Vol. XXXIX, Issue No. 135 (1959) pp. 543-545), who discloses that finely powdered crystallizable additives (e.g., nylon, isotactic polypropylene, etc.) having a melting point above that of the base polymer (e.g., low density polyethylene) and a cohesion energy per chain unit close to that of the base polymer act as nucleating agents at levels from 0.01 percent to 1 percent. Last incorporates these additives by masticating the base polymer/additive at a temperature above the melting points of the additive and the base polymer. Last forms an article of suitable shape by heating the masticated mixture to a temperature above the melting point of the base polymer. Last indicates that such articles are transparent. Last also teaches that if the article is heated beyond the melting point of the additive, the molten mixture will be optically clear only down to the crystallization temperature of the base polymer, at

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which point the transparency clouds and the benefit of the nucleation is lost.

The optical properties (e.g., clarity) of the finished polymer product can also be changed by the addition of active (chemical) nucleating agents. One
5 such organic additive clarifier, dibenzylidene sorbitol, is sold by Milliken Chemical and is trademarked MilladTM 3905. It is reportedly effective in improving haze characteristics of film made from polypropylene and
10 polyethylene.

Some nucleation agents, however, especially physical nucleation agents, adversely affect certain polymer physical properties such as tensile strength. A balance must be achieved between maintaining physical
15 properties of the polymer product with nucleators added and increasing the crystallization rate. This balance has been difficult to achieve, particularly in films.

A method has now been discovered for increasing
20 the crystallization onset temperature of a semi-crystalline thermoplastic polymer, while substantially maintaining or improving physical properties of the polymer product. The method comprises
25 blending the semi-crystalline thermoplastic polymer with at least one diluent polymer having about the same melting point as, and a density greater than or equal to, that of the semi-crystalline polymer thereby forming a polymer blend, heating the polymer blend to a point
30 above the melting point of the semi-crystalline thermoplastic polymer and the diluent polymer(s) and cooling the polymer blend to form a solid. The polymer blend can be made by dry blending or melt blending discrete polymers, or by in-situ reactor polymerization.

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In another aspect, the invention is a method of improving the optical and/or mechanical properties of fabricated objects made from a semi-crystalline thermoplastic polymer by blending with said semi-crystalline thermoplastic polymer a diluent polymer having about the same melting point as and a density greater than or equal to that of the semi-crystalline polymer to form a polymer blend, said polymer blend having an onset of crystallization temperature higher than the onset of crystallization temperature of said semi-crystalline polymer. Film Mechanical properties which can be improved include fewer breaks per unit length and high elongation at break.

The invention is also perceived as a method of improving blown film bubble stability of a semi-crystalline thermoplastic polymer by blending at least one diluent polymer having about the same melting point as and a density greater than or equal to that of the semi-crystalline polymer with said semi-crystalline polymer forming a polymer blend and extruding said polymer blend on a blown film line, said polymer blend having an onset of crystallization temperature higher than the onset of crystallization temperature of said semi-crystalline thermoplastic polymer. The frost line height of the polymer blends of the present invention is lowered resulting in a more stable blown film bubble. Cycle time of fabricating objects made using the present invention is also reduced.

Conversely, when the frost line height of a stable blown film bubble is lowered, the throughput can be increased such that the frost line height is raised back to its original level (i.e., that of the semi-crystalline polymer). Thus the invention is also a

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method of increasing throughput of a blown film line at equal frost line heights.

In still another aspect, the invention is a polymer blend comprising a semi-crystalline thermoplastic polymer blended with at least one diluent
5 polymer having about the same melting point as and a density greater than or equal to that of the semi-crystalline polymer and having a crystallization onset temperature at least about 0.1°C above the
10 crystallization onset temperature of the semi-crystalline thermoplastic polymer. The polymer blend is heated to a point above the melting point of the semi-crystalline polymer and the diluent polymer(s) and cooled to form a solid polymer blend having a
15 crystallization onset temperature at least about 0.1°C above the crystallization onset temperature of the semi-crystalline polymer.

The semi-crystalline thermoplastic polymer can
20 be any member of the known class of thermoplastic polymers and may be branched or linear. Olefinic polymers are preferred for use in the present invention as the base polymer. Low density polyethylene (LDPE),
25 also known as High Pressure Polyethylene and historically as ICI-type polyethylene, is a branched ethylene homopolymer made using free radical polymerization techniques under high pressures. The ethylene is randomly polymerized into the polymer chains
30 and forms numerous branch points. The density of LDPE is dictated by the degree and length of branches and is typically in the range of 0.91-0.925 grams per cubic centimeter (g/cm^3). The molecular weight of the LDPE is indicated by melt index (MI) as measured using ASTM D-1238 (E) (190°C/2.16 kilograms). The preferred MI range

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for LDPE is from 0.1 to 100 grams/10 minutes. The preferred semi-crystalline polymer is a linear olefinic polymer (e.g., linear polyethylene).

5 Manufacture of linear polyethylene is disclosed, e.g., in U.S. Patent 4,076,698 and involves coordination catalysts of the "Ziegler" type or "Phillips" type and includes variations of the Ziegler type, such as the Natta type. These catalysts may be used at very high pressures, but may also (and generally are) used at very low or intermediate pressures. The products made by these coordination catalysts are generally known as "linear" polymers because of the substantial absence of branched chains of polymerized monomer units pendant from the main polymer "backbone" and they are also generally known as high density polyethylene (HDPE). It is these "linear" polymers to which the present invention pertains. Linear high density polyethylene (HDPE) has a density in the range of 0.941 to 0.965 gms/cm³ while linear low density polyethylene (LLDPE) typically has a density between 0.88 grams/cubic centimeter and 0.94 grams/cubic centimeter. The density of the polyethylene is lowered by polymerizing ethylene along with minor amounts of alpha, beta-ethylenically unsaturated alkenes having from 3 to 20 carbons per alkene molecule, preferably 4 to 8 and most preferably 8 carbons per alkene molecule (i.e., 1-octene). The amount of the alkene comonomer is generally sufficient to cause the density of the linear low density polymer to be substantially in the same density range as LDPE, due to the alkyl side chains on the polymer molecule, yet the polymer remains in the "linear" classification; they are conveniently referred to as "linear low density polyethylene." These polymers retain much of the strength, crystallinity, and

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toughness normally found in HDPE homopolymers of ethylene, but the higher alkene comonomers impart high "cling" and "block" characteristics to extrusion or cast films and the high "slip" characteristic inherently found in HDPE is diminished.

5 The use of coordination-type catalysts for polymerizing ethylene into homopolymers or copolymerizing ethylene with higher alkenes to make copolymers having densities above 0.94 gms/cm^3 as defined in ASTM D-1248 (i.e., "HDPE" polymers) and/or
10 for copolymerizing ethylene with higher alkenes to make copolymers having densities in the range of LDPE and medium density polyethylene (i.e., "LLDPE" copolymers) is disclosed variously in, e.g., U.S. 2,699,457;
15 U.S. 2,862,917; U.S. 2,905,645; U.S. 2,846,425; U.S. 3,058,963 and U.S. 4,076,698. Thus, the density of the linear polyethylene useful as the semi-crystalline polymer in the present invention is from
20 0.88 g/cm^3 to 0.965 g/cm^3 . The molecular weight of the semi-crystalline polymer is indicated and measured by melt index according to ASTM D-1238 (e.g., when polyethylene is chosen as the semi-crystalline polymer, Condition (E) (i.e., $190^\circ\text{C}/2.16$ kilograms) is used to
25 determine the melt index). The melt index of the polyethylene useful as the semi-crystalline polymer can be from 0.1 grams/10 minutes to 300 grams/10 minutes, preferably from 0.1 grams/10 minutes to 50 grams/10 minutes.

30 Other semi-crystalline polymers, such as polypropylene and various ethylene and propylene terpolymers, are useful in the present invention provided the diluent polymer used in combination has about the same melting point as the semi-crystalline

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polymer. Melting points within about 10°C are defined herein as "about the same."

The diluent polymer for use in the present invention can be any polymer miscible with the semi-crystalline thermoplastic polymer, having about the same melting point as the semi-crystalline polymer and a density greater than or equal to that of the semi-crystalline thermoplastic polymer. The preferred semi-crystalline thermoplastic polymer is a linear olefinic polymer (e.g., linear low density polyethylene). The most preferred linear olefinic polymer is a high density polyethylene polymer. The HDPE has a density between 0.94 grams/cubic centimeter and 0.965 grams/cubic centimeter and a melt index between 0.01 grams/10 minutes and 3000 grams/10 minutes, preferably between 50 grams/10 minutes and 300 grams/10 minutes. The HDPE can be a homopolymer of ethylene, or it can be a copolymer of ethylene with minor amounts of at least one alpha, beta-ethylenically unsaturated alkene having from 3 to 20 carbons per alkene molecule. Amounts of the diluent polymer added to the semi-crystalline polymer will vary, depending upon the type of diluent polymer and the type of semi-crystalline polymer chosen, but will generally be less than about 50 percent, preferably less than about 20 percent, more preferably less than about 10 percent, and as low as about 0.01 percent by weight of the total blend, with the balance of the blend comprising the semi-crystalline polymer. The semi-crystalline polymer and the diluent polymer together can contain minor amounts of additives (e.g., antioxidants, pigments) which do not interfere with the nucleation of the polymer blend.

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Articles made from the blends of the present invention include blown film (e.g., that made with Internal Bubble Cooling (IBC) or a dual lip air ring), cast film, melt spun fibers, and other processes requiring thermal processing of polymers and subsequent cooling.

EXPERIMENTAL

Blends of the semi-crystalline polymer and the diluent polymer are made by dry blending, melt blending discrete polymers, or by in-situ reactor polymerization. Dry blending pellets can be accomplished by any convenient means, e.g., tumble blending weighed portions of pellets in fibre packs. Since pellet stratification can occur in dry blends while in transit, melt blending is preferred. Melt blending can be accomplished by feeding a dry blend (made as described above) into an extruder/compounder line equipped with a pelletization system (e.g., an underwater pelletizer, or a water trough through which the reextruded strands are cooled and later chopped into pellets). Blends formed by in-situ reactor polymerization can be made by side-arm extrusion of the diluent polymer into the molten semi-crystalline polymer stream just prior to pelletization, or the blends can be made by operating multiple reactors such that the diluent polymer and the semi-crystalline polymer are each made and blended immediately after polymerization, before or after removal from the reactor(s), but prior to pelletization in a single continuous system. Such multiple reactor operation is disclosed, for example, in U.S. Patent 3,914,342. There are several ways known to skilled artisans for making in-situ polymerized reactor blends, and the invention is not limited to any one of the methods.

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The crystallization onset temperatures of the blend components and of the blends of the present invention are measured using DSC. Each sample to be tested is made into a compression molded test plaque according to ASTM D 1928. The plaques are then
5 microtomed at room temperature using a Reichert Microtome or razor blade to obtain samples having a thickness of about 15 microns. About 5 milligrams of each sample to be tested is placed in the DSC pan and
10 heated to about 180°C, held at that temperature for 3 minutes to destroy prior heat history, cooled to 25°C at a rate of 10°C/minute and held at that temperature for 2 minutes. The crystallization onset temperature and the
15 peak temperature are recorded by the DSC as the temperature at which crystallization begins and the temperature at which the sample is as fully crystallized as possible, respectively, during the cooling period
from 180°C to 25°C. The sample is then heated again from 25°C to 140°C at a rate of 10°C/minute to record the heat
20 of fusion and calculate total percent crystallinity. For polyethylene, the percentage crystallinity is obtained using the latent heat of fusion equal to 292 Joules/gram for 100 percent crystalline polyethylene.

25

Example 1

An ethylene/1-octene LLDPE copolymer having a melt index of 2.3 grams/10 minutes and a density of 0.917 g/cm³ (designated the semi-crystalline
30 thermoplastic polymer), an ethylene/1-octene HDPE copolymer having a melt index of 105 grams/10 minutes and a density of 0.953 g/cm³ (designated the diluent polymer) and three blends of these two polymers were made into compression molded plaques as described previously. The blends were made by tumble blending the

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pellets together at room temperature and then feeding the dry blend into a Henschel mixer by mass balance in the following weight percent proportions:

- 100 percent semi-crystalline: 0 percent diluent;
- 5 96 percent semi-crystalline: 4 percent diluent;
- 92 percent semi-crystalline: 8 percent diluent and
- 10 0 percent semi-crystalline: 100 percent diluent.

The mixer is in the hopper of a 4 inch (10 cm) screw extruder through which the samples were run and melt blended. Other forms of melt blending are also

15 acceptable. Films having a thickness of about 0.8 mils (20 micrometers) were fabricated on an EGAN cast film line according to the conditions outlined in Table I and subsequently evaluated for number of breaks per thousand feet on a LANTECH pallet wrapper. The LANTECH pallet

20 wrapper prestretched the film to test the film's effectiveness in holding the goods together (e.g., a pallet of boxes). The LANTECH prestretches film so that the film shrinks slightly to hold the goods together.

25 Table II lists the breaks per one thousand feet (305 meters) for 100 percent semi-crystalline polymer and for each of the polymer blends at 250 percent and 300 percent prestretch.

30

TABLE I
FABRICATION CONDITIONS FOR SAMPLES

5	Extruder Zone 1 (°C/°F)	254/490
	Extruder Zone 2 (°C/°F)	260/500
	Extruder Zone 3 (°C/°F)	277/530
10	Gate (°C/°F)	288/550
	Adapter (°C/°F)	288/550
	Die Zone 1(°C/°F)	288/550
	DieZone 2 (°C/°F)	288/550
15	90° Adapter (°C/°F)	288/550
	Feedblock (°C/°F)	288/550
	Melt Temp. (°C/°F)	277/530
	Chill Roll (°C/°F)	13/56
20	Extruder (rpm)	68
	Film Gauge (micrometers/mils)	20/.8
	Pressure (MPa/psi)	9.30/1350
	Line Speed (feet/minute)	850 (259m/min)
25	Through put (lbs/hr)	350 (159 kg/hr)
	Die Width (inches)	30 (76 cm)
	Die Gap (mils)	15 (375 micrometers)

TABLE II

5	Polymer blend proportions (percent semi-crystalline: percent diluent)	Breaks per 1000 feet (305 m) at 250 percent prestretch	Breaks per 1000 feet (350 m) at 300 percent prestretch
	100:0	20	19
	96:4	2	2
	92:8	3	3
10	0:100	NM	NM

NM = Not Measured; film could not be formed from this polymer.

15 Films made from the blends of the present invention had fewer breaks per 1000 feet (305 m) than the semi-crystalline polymer alone.

20 The measured crystallization onset temperature and DSC peak temperature (both measured as described in EXPERIMENTAL) of samples of each of these blends and of the individual blend components are listed in Table III. The predicted crystallization onset temperature and DSC peak temperature of the blends are mathematically
25 linearly calculated based on the percentages of each component and that component's measured properties and are also listed in Table III. The measured melting point for the semi-crystalline polymer was about 122°C and about 127.83°C for the diluent polymer.

30

TABLE III

Polymer blend proportions (percent semi-crystalline: percent diluent)	Measured cryst. onset temp. (°C)	Predicted cryst. onset temp. (°C)	Measured DSC cryst. peak temp. (°C)	Predicted DSC cryst. peak temp. (°C)
100:0	105.9	NA	103.2	NA
96:4	106.9	106.4	103.1	103.7
92:8	110.1	106.9	106.9	104.1
0:100	118.6	NA	114.2	NA

NA = Not Applicable; measured reference point.

As Table III indicates, polymer blends of a semi-crystalline polymer and a diluent polymer of the present invention had a higher measured crystallization onset temperature than that predicted for the polymer blend. Thus when combining a semi-crystalline polymer with a diluent polymer according to the present invention, a synergistic effect was evident, causing the polymer blend to nucleate earlier and to accelerate crystallization.

Example 2

An ethylene/1-octene LLDPE copolymer having a melt index of 1 gram/10 minutes and a density of 0.92 g/cm³ (designated the semi-crystalline thermoplastic polymer), an ethylene/1-octene HDPE copolymer having a melt index of 65 grams/10 minutes and a density of 0.953 g/cm³ (designated the diluent polymer), were made into a blend having about 4.3 percent by weight diluent polymer by preparation in a reactor system. This polymer blend and another polymer (designated the comparative polymer) having about the same basic physical properties as the polymer blend were each made

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into thin gauge blown film on a STERLING Blown Film Line. This line has a 3.5 inch (8.9 cm) diameter extruder, L/D=30:1, an 8 inch (20 cm) diameter Western Polymer die with a 70 mil (1750 micrometers) die gap, a STERLEX barrier type screw and Internal Bubble Cooling (IBC).

Physical properties of the polymer blend and the comparative polymer appear in Table IV. The measured melting point for the semi-crystalline thermoplastic polymer was about 120.69°C, about 128.15°C for the diluent polymer, about 121.06°C for the polymer blend and about 120.69°C for the comparative polymer.

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Table IV

Polymer	Melt Index (grams/10 minutes)	Density (g/cm ³)	Measured cryst. onset temp. (°C)	Predicted cryst. onset temp. (°C)	Measured DSC cryst. peak temp. (°C)	Predicted DSC cryst. peak temp. (°C)
Blend	1.04	0.9217	110.93	110.3	108.53	108.31
Comp.*	1.03	0.9203	109.91	NA	108.03	NA

* Comp. = Comparative polymer
NA = Not Applicable

Each polymer was processed using the same extruder melt profile described in Table V below:

Table V

Zone	1	2	3	4	5	Adapt. 1	Adapt. 2	Die 1	Die 2
Temp. (°F)	350 (177°C)	425 (218°C)	400 (204°C)	350 (177°C)	350 (177°C)	450 (232°C)	450 (232°C)	450 (232°C)	480 (249°C)

Additional line conditions and the resultant film parameters for each polymer appears in the following table:

Table VI

	Polymer	
	Blend	Comparative
Feed Pressure (psi)	3580 (25 MPa)	3730 (26 MPa)
Screw RPM	50	50
Melt Temperature	430 °F (221°C)	436 °F (224 °C)
Lay Flat (inches)	31.5 (80 cm)	31.5 (80 cm)
Blow-up Ratio (Film diameter/ Die diameter)	2.5	2.5
Line speed (feet/min.)	285 (87 m/min)	285 (87 m/min)
Amps	144	150
Pounds per Hour	345 (156 kg/hr)	345 (156 kg/hr)

Table VII contains comparative data relating properties of 0.6 mil (15 micrometers) gauge blown film made from each of these polymers.

As the data indicate, the polymer blend of the present invention had a measured crystallization onset temperature higher than the comparative polymer.

Table VII

Polymer	45° Gloss (ASTM D 2457)	Film Clarity (ASTM D 1746**)	Film Haze (ASTM D 1003)	Frost Line Height (inches)	Throughput at equal frost line heights (lbs./hour)
Blend	41.11	46.30	11.94	28 (71 cm)	381 (173 kg/hr)
Comp.*	34.03	20.12	18.04	33 (84 cm)	370 (168 kg/hr)

* Comp. = Comparative polymer

** Conditioning time modified to 30 minutes

Film made from the polymer blend of the present invention had better gloss, better clarity and better haze characteristics than film made from the comparative polymer.

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CLAIMS:

1. A method of increasing the crystallization onset temperature of a semi-crystalline thermoplastic polymer comprising the steps of:

5 (a) blending with the semi-crystalline polymer at least one diluent polymer, wherein the diluent polymer is characterized as having a melting point within 10°C of, and a density greater than or equal to, that of the semi-crystalline polymer, thereby forming a polymer blend,

10 (b) heating the polymer blend above the melting points of the semi-crystalline polymer and the diluent polymer(s), and

(c) subsequently cooling the polymer blend until solid, thereby forming a cooled polymer blend.

15

2. The method of Claim 1 further comprising the steps of:

20 (d) measuring the crystallization onset temperature of the semi-crystalline thermoplastic polymer, and

(e) adding an amount of the diluent polymer sufficient to increase the crystallization onset temperature of the semi-crystalline thermoplastic polymer by at least about 0.1°C.

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3. The method of Claim 1 wherein the polymer blend is made by blending discrete polymers.

4. The method of Claim 1 wherein the polymer blend is made by in-situ reactor polymerization.

5

5. The method of Claim 1 wherein the semi-crystalline thermoplastic polymer is an olefinic polymer.

10

6. The method of Claim 5 wherein the olefinic polymer is a linear polyethylene characterized as an ethylene/ C₃-C₂₀ alpha, beta-ethylenically unsaturated alkene copolymer.

15

7. The method of Claim 5 wherein the olefinic polymer is a low density polyethylene.

20

8. The method of Claim 1 wherein the diluent polymer is an olefinic polymer.

9. The method of Claim 8 wherein the diluent polymer is a high density polyethylene.

25

10. The method of Claim 5 wherein the linear polyethylene is an ethylene/1-octene copolymer characterized as having a density between 0.88 grams/cubic centimeter and 0.96 grams/cubic centimeter and a melt index between 0.1 grams/10 minutes and 50 grams/10 minutes.

30

11. The method of Claim 10 wherein the diluent polymer is a high density polyethylene characterized as

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having a density between 0.95 grams/cubic centimeter and 0.97 grams/cubic centimeter and a melt index between 0.01 grams/10 minutes and 3000 grams/10 minutes.

12. The cooled polymer blend obtainable by the method of Claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11.

13. A method of extruding a thermoplastic polymer into blown film, wherein the thermoplastic polymer is characterized as a polymer blend of a linear low density polyethylene and at least one diluent polymer having a melting point within 10°C of, and a density greater than or equal to, that of the linear low density polyethylene, thereby increasing throughput of the polymer blend over that of the linear low density polyethylene alone.

14. The method of Claim 13 wherein the polymer blend has an onset of crystallization temperature higher than the onset of crystallization temperature of the linear low density polyethylene alone.

15. The blown film formed by the method of Claim 13.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/08224

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁸ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 08 L 23/08, C 08 L 23/06																	
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="padding: 5px;">IPC⁵</td> <td style="padding: 5px;">C 08 L 23/00</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁶</div>			Classification System	Classification Symbols	IPC ⁵	C 08 L 23/00											
Classification System	Classification Symbols																
IPC ⁵	C 08 L 23/00																
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category ¹⁰</th> <th style="border-bottom: 1px solid black;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 15%; border-bottom: 1px solid black;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">JOURNAL OF POLYMER SCIENCE, vol. 39, issued 1959, A.G.M. LAST "Nucleation effects in high polymers", see pages 543-545 (cited in the application). --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1, 3, 5, 7, 8</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 3 966 845 (VAN BREDERODE et al.) 29 June 1976 (29.06.76), see claims. --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1, 3, 5</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A1, 0 068 773 (MILLIKEN RESEARCH CORPORATION) 05 January 1983 (05.01.83), see page 1, lines 3-33. --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A2/A3, 0 080 198 (THE DOW CHEMICAL COMPANY) 01 June 1983 (01.06.83), see page 8, line 12 - page</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1, 3, 5-15</td> </tr> </tbody> </table>			Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	JOURNAL OF POLYMER SCIENCE, vol. 39, issued 1959, A.G.M. LAST "Nucleation effects in high polymers", see pages 543-545 (cited in the application). --	1, 3, 5, 7, 8	A	US, A, 3 966 845 (VAN BREDERODE et al.) 29 June 1976 (29.06.76), see claims. --	1, 3, 5	A	EP, A1, 0 068 773 (MILLIKEN RESEARCH CORPORATION) 05 January 1983 (05.01.83), see page 1, lines 3-33. --	1	A	EP, A2/A3, 0 080 198 (THE DOW CHEMICAL COMPANY) 01 June 1983 (01.06.83), see page 8, line 12 - page	1, 3, 5-15
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁴ Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 50%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search <div style="text-align: center;">30 March 1992</div> </td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center;">21.04.92</div> </td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;"> International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="border-bottom: 1px solid black; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center;"> Els Vonk </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center;">30 March 1992</div>	Date of Mailing of this International Search Report <div style="text-align: center;">21.04.92</div>	International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center;"> Els Vonk </div>											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
	16, line 26. ---	
A	EP, A2, 0 168 928 (BCL LIMITED) 22 January 1986 (22.01.86), see claims 1-7; table 1. ---	1,3,5- 7,13, 15
A	US, A, 3 998 914 (LILLIS et al.) 21 December 1976 (21.12.76), see column 1, line 5 - column 4, line 54. ----	1,3,5, 7-9, 11-15

ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/US 91/08224 SAE 54756

In diesem Anhang sind die Mitglieder
der Patentfamilien der in obenge-
nannten internationalen Recherchenbericht
angeführten Patentdokumente angegeben.
Diese Angaben dienen nur zur Unter-
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
national search report. The Office is
in no way liable for these particulars
which are given merely for the purpose
of information.

La présente annexe indique les
membres de la famille de brevets
relatifs aux documents de brevets cités
dans le rapport de recherche inter-
national visée ci-dessus. Les renseigne-
ments fournis sont donnés à titre indica-
tif et n'engagent pas la responsabilité
de l'Office.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche			Datum der Veröffentlichung Publication date Date de publication		Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets		Datum der Veröffentlichung Publication date Date de publication	
US A	3966845		29-06-76		US A	3886227	27-05-75	
EP A1	68773		05-01-83		US A	4419473	06-12-83	
					AT E	17949	15-02-86	
					CA A1	1263985	19-12-89	
					DE C0	3269057	27-03-86	
					EP B1	68773	12-02-86	
					JP A2	58021437	08-02-83	
					JP B4	61038941	01-09-86	
EP A2	80198		01-06-83		AU A1	90156/82	31-05-84	
					CA A1	1189218	18-06-85	
					EP A3	80198	07-03-84	
					GB A1	2110700	22-06-83	
					GB B2	2110700	12-06-85	
					HK A	217/86	04-04-86	
					JP A2	58098376	11-06-83	
					MY A	534/86	31-12-86	
					US A	4542188	17-09-85	
					US A	4664866	12-05-87	
EP A2	168928		22-01-86		EP A3	168928	04-03-87	
					GB A0	8412960	27-06-84	
					GB A0	8512810	26-06-85	
					GB A1	2159091	27-11-85	
					GB B2	2159091	18-03-87	
US A	3998914		21-12-76		CA A1	957796	12-11-74	
					DE A1	2304998	09-08-73	
					GB A	1413379	12-11-75	
					GB A	1413380	12-11-75	